Brazilian Journal
of Chemical
Engineering

ISSN 0104-6632
Printed in Brazil
www.abeq.org.br/bjche

Vol. 24, No. 02, pp. 00 - 00, April - June, 2007

RHEOLOGY AND PHASE BEHAVIOR OF AGGREGATING EMULSIONS RELATED TO DROPLET-DROPLET INTERACTIONS

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(Received: January 10, 2006 ; Accepted: November 11, 2006)

Abstract - The present work deals with the relationship between colloidal interactions and physical properties of emulsions, in particular rheology and gel transition. Experimental data on protein-stabilized oil-in-water emulsions are considered. In this system, the excess of protein in the aqueous phase yields reversible droplet aggregation by the mechanism of depletion. Thus both phase and flow behaviors can be controlled by changing protein concentration, ionic strength and temperature. Calculations of the potential of interaction between droplets are carried out in the framework of colloid science. Particular emphasis is placed on the role that droplet-droplet interaction plays in defining the morphology of the aggregates, hence the microstructure and finally, the bulk physical properties. This understanding offers new perspectives in the study of complex food systems.
Keywords: Emulsions; Colloidal interactions; Aggregation; Gelation; Viscosity.

INTRODUCTION

Colloidal dispersions have phase transitions from fluid to solid-like states, which can be characterized by rheometric measurement. Nevertheless, the lack of a coherent understanding of the phenomena involved usually led to semiempirical interpretations. The conceptual framework proposed in the recent literature clearly defines the role of particle concentration, interaction forces and shear stress in the aggregation and gelation of colloids (Trappe et al., 2001; Dawson, 2002; Bergenholtz et al., 2003). Relevant efforts have also been made to attain quantitative predictions of the rheometric functions in terms of colloidal interactions (see, for instance, Quemada and Berli, 2002). This knowledge is of primary importance in the food industry, where the physical properties of colloidal dispersions are generally controlled by adjusting the formulation. More precisely, in the case of protein-stabilized emulsions, both rheology and phase behaviors are determined by the interaction forces between droplets (Dickinson, 1998; Blijdenstein et al., 2003; Dimitrova et al., 2004; Tadros, 2004).

Emulsions prepared with sodium caseinate constitute a model system to study the effect of these interactions on flow behavior. In particular, excess protein in the aqueous phase yields reversible droplet aggregation by the mechanism of depletion. Thus the strength of the droplet-droplet attraction can be controlled by changing protein concentration, ionic strength and temperature. Previous work reported the

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viscosity (Berli et al., 2002) and gel transition (Berli et al., 2003) displayed by these emulsions. The aim of the present work is to illustrate how the knowledge of interaction forces between particles can help one to understand, and hence better exploit, the macroscopic behavior of these relatively complex fluids. For this purpose, the main characteristics of the emulsions are briefly described in the following section. Then, an overview of theoretical aspects concerning colloidal interactions, gelation and rheology is presented. Finally, the flow curves and phase diagrams of these emulsions are discussed in relation to the droplet-droplet interaction potential.

SAMPLE CHARACTERISTICS

Oil-in-water emulsions prepared with calcium-free sodium caseinate as emulsifier are considered. The preparation and physicochemical characterization of these emulsions were reported in previous work (Berli et al., 2002); the main features are mentioned here. The volume fraction of oil was $\phi = 0.30$. The aqueous phase was a 20:80 mixture of ethanol and water. Samples were prepared with protein concentrations C_p varying between 20 and 60 g/kg. In practice, $C_p \approx 15$ g/kg was sufficient to fully cover the oil droplets and the emulsions were stable for several months. The excess protein formed submicelles in the aqueous phase, with an average radius $b \approx 5$ nm. Oil droplets had an average radius $a = 190$ nm, as measured by small angle light scattering (monomodal droplet size distribution). In a series of samples, the ionic strength was increased by adding NaCl 12.5 mM.

Therefore, these emulsions are multicomponent systems consisting of protein-covered oil droplets, free protein, salt, ethanol and water. Despite this complexity, from a rheological point of view, the system is considered as a dispersion of spherical particles (oil droplets) in a Newtonian fluid of viscosity η_F, which is, in turn, a dilute solution of small particles (casein submicelles) in ethanol/water. Thus emulsions are regarded as colloid-polymer mixtures, taking into account that oil droplets behave as hard spheres under flow (Berli et al., 2002). The viscosity curves $\eta(\sigma)$ were determined for a series of imposed shear stresses σ by using a stress-controlled rheometer with a cone-plate cell. This work includes data on viscosity at different temperatures (not reported in the previous work).

Another aspect relevant to mention is that droplet aggregation, which increases the size of the kinematic units, may enhance phase separation due to creaming. Indeed, in aggregating emulsions both flocculation and creaming occurs, and the final state of the system depends on the relative rate of the processes. Basically, when the aggregation rate is significantly higher than the creaming rate, a network spanning throughout the fluid will form, and hence a phase transition (gelation), rather than phase separation, is attained (Dickinson, 1998; Blijdenstein et al., 2003). This is the case of the emulsions considered here, where the rate of creaming is negligible.

THEORETICAL BACKGROUND

Droplet-Droplet Interactions

The first interaction to be accounted for is the attraction due to the London-van der Waals dispersion forces. For spherical particles with radius a, separated by a center-to-center distance R, the potential energy is

$$U_A = -\frac{A_H}{6}\left[\frac{2a^2}{R^2-4a^2}+\frac{2a^2}{R^2}+\ln\left(1-\frac{2a^2}{R^2}\right)\right] \qquad (1)$$

where $A_H \approx 4\text{x}10^{-21}$ J is the Hamaker constant for oil droplets in aqueous media (Israelachvili, 1997). This droplet-droplet attraction is counterbalanced by repulsive forces originating at the oil-water interface. In fact, the casein tails exposed to the solvent are electrically charged, and hence a repulsive interaction arises as the electrical double layers surrounding the droplets overlap. The potential energy is

$$U_R = 2\pi\varepsilon\psi_0^2 a \ln\left[1+\exp\left(-\frac{R-2a}{\lambda}\right)\right] \qquad (2)$$

for $a/\lambda >> 1$, where λ is the Debye length, evaluated from the salt content in the aqueous phase. Also in Eq. (2), $\varepsilon \approx 6.1\ 10^{-10}$ C^2/Nm^2 is the permittivity of the ethanol/water mixture and $\psi_0 \approx 40$ mV is the surface potential of protein-covered droplets (see Berli et al., 2002 and references therein). Equations (1) and (2) constitute the well-known DLVO pair potential.

When emulsions are prepared with excess protein (C_p > 20 g/kg) and submicelles are formed, flocculation is generally observed (see, for example, Dickinson, 1998). In fact, short-range repulsive forces yield a minimum distance of approach between droplets and submicelles, which are assumed to interact with an equivalent hard-sphere radius L. When droplets approach one another and the surface-to-surface distance becomes $R - 2a < 2L$, the depletion of submicelles in the interdroplet zone generates an attractive force between droplets due to entropic effects. The potential energy of this interaction is (Jenkins and Snowden, 1996)

$$U_D = -\frac{4}{3}\pi \; a_L^3 \;\; \Pi\left(1 - \frac{3R}{4a_L} + \frac{R^3}{16a_L^3}\right) \qquad (3)$$

for $2a < R < 2a_L$ and vanishes for $R \geq 2a_L$, where $a_L = a + L$. In Eq. (3), the osmotic pressure of the bulk Π is an increasing function of C_p and is included by considering the nonideality of the protein solution (Berli et al., 2002). In addition, since submicelles are electrostatically charged, the exclusion radius is introduced as $L = b + \beta\lambda$, where β is a constant of order unity and λ accounts for the effect of ionic strength. Finally, the total pair potential, as a function of interparticle distance, is estimated as $U(R) = U_A + U_R + U_D$ by using Eqs. (1), (2) and (3), respectively.

Aggregation and Gelation

Colloidal particles undergo Brownian motion as driven by the thermal energy k_BT (k_B is the Boltzmann constant and T the absolute temperature). When the interaction potential U(R) involves an attractive minimum, the magnitude of which (U_w) is similar or higher than k_BT, flocculation takes place. At low ϕ, the aggregates move freely through the medium and the suspension remains fluid. As ϕ increases, particle clusters overlap and the system displays a solid-like behavior. In suspensions of noninteracting hard spheres, this fluid-to-solid transition occurs when ϕ reaches the glass transition volume fraction, $\phi_G \approx 0.58$. At this concentration, particles are trapped in transient cages formed by their nearest neighbors and diffusion is no longer possible (see Quemada and Berli, 2002, for further discussions on this aspect). Similarly, the gelation of aggregating colloids has been suggested to occur when diffusing clusters become crowded (Segrè et al., 2001). In this case, the effective volume fraction of the disperse phase is $\phi_{eff} > \phi$, since it includes not only the volume occupied by the particles, but also the volume of solvent immobilized hydrodynamically in the flocs. Therefore, if the aggregated suspension becomes solid-like when ϕ_{eff} reaches ϕ_G, the critical concentration for gel transition may be written $\phi_c \approx \phi_G(\phi / \phi_{eff})$. This framework comprises colloid-polymer mixtures (Trappe et al., 2001; Dawson, 2002; Bergenholtz et al., 2003).

The gel transition can also be reached by increasing the strength of particle-particle "bonds" at a given value of ϕ (Trappe et al., 2001; Trappe and Sandkühler, 2004). This remarkable feature of flocculated suspensions can be accounted for as a diminution of ϕ_c with the strength of the interaction (Segrè et al., 2001). For the case of aggregating emulsions considered here, data are well correlated through

$$\phi_c = \phi + (\phi_c^* - \phi) \;\; \exp\left(-\frac{\alpha U_w}{k_B T}\right) \qquad (4)$$

where α is a dimensionless parameter of order unity and ϕ_c^* represents a critical concentration for the suspension of fully dispersed droplets (Berli et al., 2003). Therefore, the gel transition can be attained either by increasing ϕ at a constant U_w or by increasing U_w at a constant ϕ. The second possibility is explored here through depletion flocculated emulsions, where the "bond" energy is modified by varying protein concentration, ionic strength and temperature at $\phi = 0.3$.

Rheology

The considerations above hold under quiescent conditions. When a shear stress is applied, flocculated emulsions show strong shear thinning due to the gradual breakup of aggregates induced by shear. The viscosity curves of these emulsions are described through the following viscosity model (Quemada and Berli, 2002):

$$\eta(\sigma) = \eta_\infty \left(\frac{1 + \sigma/\sigma_C}{(\eta_\infty/\eta_0)^{1/2} + \sigma/\sigma_C}\right)^2 \qquad (5)$$

where η_0 and η_∞ are the limiting viscosities for $\sigma \to 0$ and $\sigma \to \infty$, respectively. Thus η_0 characterizes the viscosity of aggregated emulsions, while η_∞ represents the fully disaggregated system (individual droplets) due to the effect of shear stress. For colloidal dispersions with attractive forces between particles, the critical shear stress is

$$\sigma_C = \frac{k_B T}{a^3}\left(1 + \frac{U_w}{k_B T}\right) \tag{6}$$

which provides a simple connection between the interparticle "bond" energy and the macroscopic viscosity.

In addition, the low shear viscosity of concentrated dispersions is related to the particle volume fraction by

$$\frac{\eta_0}{\eta_F} = \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \tag{7}$$

where ϕ_m is the maximum packing fraction (Quemada and Berli, 2002). According to this equation, the viscosity diverges when ϕ approaches ϕ_m or, equivalently, when the system reaches the fluid-to-solid transition. Therefore, assuming $\phi_c \approx \phi_m$, the critical volume fraction for gelation can be estimated from viscosity data at $\sigma \to 0$, where the microstructure is not affected significantly by shear.

RESULTS AND DISCUSSIONS

Interaction Potentials

The interaction energy between droplets predicted by Eqs. (1)-(3) is shown Figure 1a. The presence of depletion attraction yields the secondary minimum observed in U(R) (the negative part of the curve). Otherwise, for the emulsions considered here, the DLVO interaction predicts a purely repulsive potential (positive part of the curve), except for the primary minimum at R ~ 2a. It is readily seen in Figure 1a that the secondary minimum is enhanced when protein concentration increases. In fact, the depth of the potential well, $U_w = |U(R_w)|$, is controlled by protein concentration, while the position of the minimum, R_w, depends mainly on the salt content (the ionic strength of the aqueous phase increases with C_p, leading to a decrease in λ, L and R_w). The effect of varying temperature is not simple to infer a priori because A_H, ε, λ, ψ_0 and Π are involved. Given these potential curves, one knows that the force between particles ($F = -\partial U/\partial R$) is attractive for $R > R_w$ and repulsive for $R < R_w$. Consequently, droplets stay preferably in the potential well of their neighbors, forming aggregates. The macroscopic consequences of this are observed in Figure 1b, where the emulsion viscosity curves are presented.

Shear Flow Behavior

Figure 1b shows that, when the caseinate concentration in the aqueous phase is low, the emulsions are almost Newtonian with low viscosity values. As the caseinate concentration increases, the viscosity $\eta(\sigma \to 0)$ increases more than two orders of magnitude. For higher shear stresses, $\eta(\sigma)$ decreases abruptly due to the diminution of the mean size of aggregates. In fact, droplet aggregation is easily reverted by applying the mechanical energy necessary to break up the "bonds", i.e., $\sigma a^3 \sim U_w$. It is worth noting here that Figures 1a and b illustrate the close relationship that exists between the droplet-droplet interaction and the rheological response of the emulsions. Based on this knowledge, Figure 1c adds some speculations about the structure of the aggregates formed at different values of C_p.

Apart from protein concentration, the interaction potential also depends on ionic strength and temperature. The effect of these variables on the viscosity curves can be analyzed through the parameter σ_C, which roughly determines the transition between a suspension of aggregates and a suspension of dispersed droplets. Indeed, when a given σ is applied, an aggregation-disaggregation equilibrium is established, in which the forward (depletion-induced clustering) and the backward (shear-induced breakup) processes balance. The viscosity model captures these phenomena through a kinetic description of the microstructure (Quemada and Berli, 2002). This is confirmed in Figure 2, where it is shown that viscosity curves of emulsions with different protein concentrations, ionic strengths and temperatures are superposed over a master curve when the reduced viscosity $\eta_{red} = (\eta^{-1/2} - \eta_\infty^{-1/2})/(\eta_0^{-1/2} - \eta_\infty^{-1/2})$ is plotted against σ/σ_C, in accordance with Eq. (5). For these calculations, the parameters η_0, η_∞ and σ_C had been previously obtained for every curve $\eta(\sigma)$, by fitting Eq. (5) to experimental data η vs. σ (Berli et al., 2002). The procedure is carried out by using standard mathematical software. As mentioned above, data measured at T < 20°C had not been reported before.

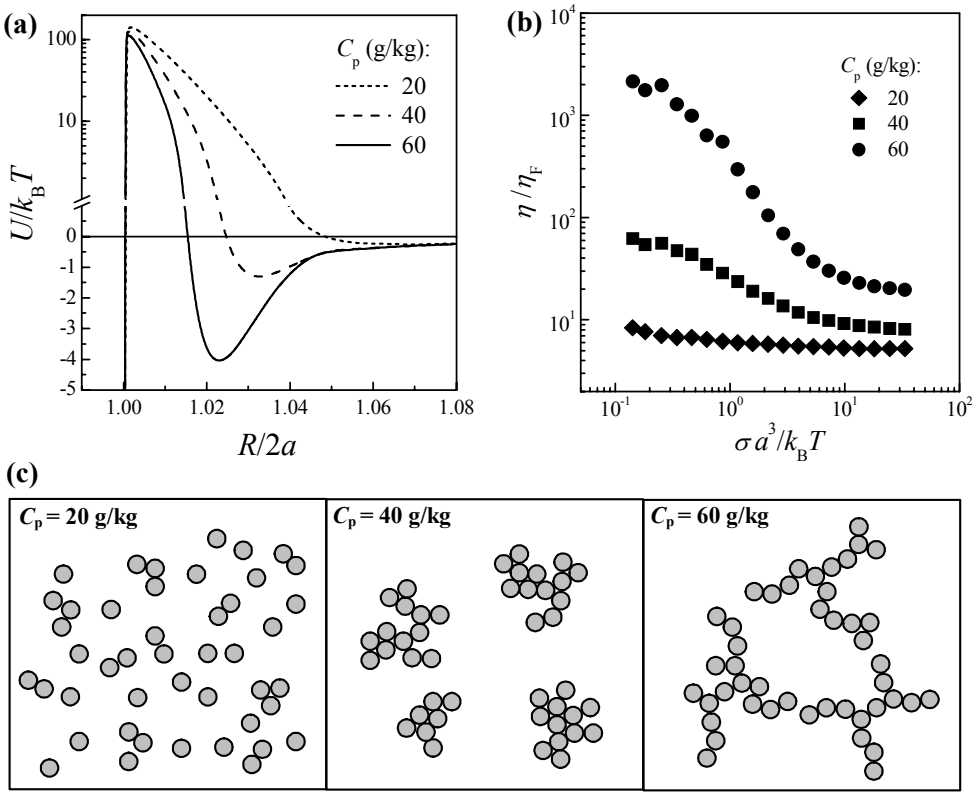

Figure 1: (a) Dimensionless pair interaction predicted by Eqs. (1)-(3) as a function of the relative interparticle distance. Data for numerical calculations are (apart from those reported in the text): C_p = 20 g/kg, Π = 58.7 Pa, a/λ = 63; C_p = 40 g/kg, Π = 309 Pa, a/λ = 89; C_p = 60 g/kg, Π = 585 Pa, a/λ = 109; T = 20°C. (b) Emulsion viscosity, relative to that of the aqueous phase, as a function of the dimensionless shear stress for different protein concentrations (ϕ = 0.3, no salt added, T = 20°C). (c) Schematic representations of particle aggregates for different protein concentrations.

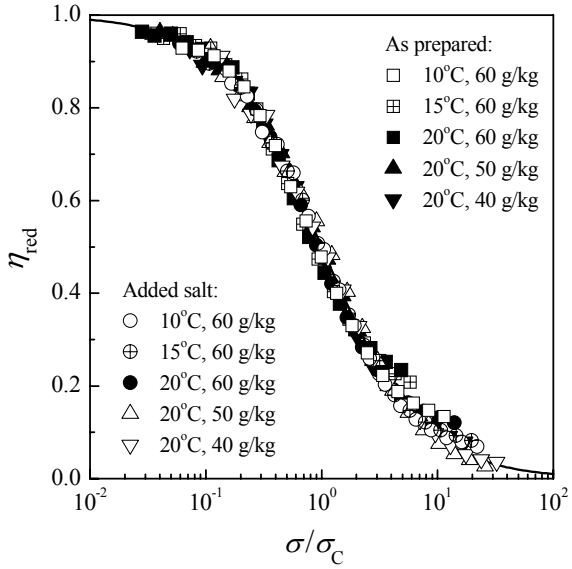

Figure 2: Reduced viscosity (see definition in the text) as a function of the relative shear stress for oil-in-water emulsions with ϕ = 0.3 and different protein concentrations, ionic strengths and temperatures. Emulsions with "added salt" include NaCl 12.5 mM. The full line is the prediction of Eq. (5).

Phase Behavior

In this section, the relation between the critical concentration for gelation and the strength of the attractive interaction is analyzed. For this purpose, the values of U_w and ϕ_c were estimated from viscosity data reported in Figure 2 by using Eqs. (5)-(7). Figure 3 clearly shows that the higher the attractive interaction, the lower the critical concentration for gelation. In fact, high values of ϕ are required to reach the gelation threshold when the depletion attraction is weak ($U_w/k_BT < 1$), since droplet aggregation is negligible. At the other extreme, when the interaction is strong ($U_w/k_BT >> 1$), droplet aggregation yields large clusters, and hence low values of ϕ are enough to attain a particle network spreading throughout the sample.

Figure 3 constitutes a phase diagram for the aggregated emulsions, since data plotted defines the boundary between fluid and solid-like states. It should be mentioned that typical diagrams of colloid-polymer mixtures are usually presented as volume fraction vs. polymer concentration (see, for instance, Bergenholtz et al., 2003). On the basis of the quantitative correlation given by Eq. (4), the diagram in Figure 3 incorporates the effects of ionic strength and temperature as well, thus providing a generalized description of the phase line (see also Trappe and Sandkühler, 2004).

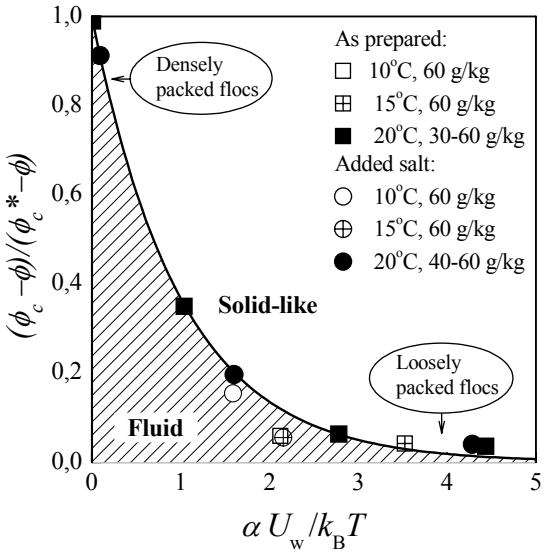

Figure 3: Phase diagram for oil-in-water emulsions with $\phi = 0.3$ and different protein concentrations, ionic strengths and temperatures. The phase line is given by Eq. (4) with the following parameter values: As prepared, $\alpha = 1.1$, $\phi_c^* = 0.4$; added salt, $\alpha = 3.1$, $\phi_c^* = 0.36$.

Implications of the Potential Curve

The results discussed in previous sections allow one to infer the underlying mechanisms that govern the shear thinning and gel transition of protein-stabilized emulsions. For further analysis, it is relevant to consider the characteristics of the U(R) pair interaction, obtained as the superposition of DLVO and depletion interactions (Eqs. (1)-(3)). As mentioned above, particles remain preferably at the minimum potential energy, where $F = -\partial U(R)/\partial R$ is attractive for $R > R_w$ and repulsive for $R < R_w$. Due to the form of U(R) in close vicinity of the minimum, it may be illustrative to think of the interaction force between particles at $R \approx R_w$ as that produced by an equivalent spring, the equilibrium length of which is R_w. The second derivative of the potential at $R \approx R_w$ provides a sense of the stiffness of the hypothetic spring, i.e., $\partial^2 U(R_w)/\partial R^2 \sim k_w$, where k_w is the equivalent spring constant (Potanin et al., 1995). In addition, to interpret the effect of cluster morphology, it may be assumed that (i) aggregates are roughly spherical with an effective radius R_{eff} and (ii) the cluster structure is self-similar (Lin et al., 1989). Thus one may write $\phi_{eff} \approx \phi(R_{eff}/a)^{3-f}$, where the fractal dimension f accounts for cluster compactness.

Figure 1a shows that at low values of C_p the secondary minimum is shallow and wide: $U_w < k_BT$ and k_w is relatively low (bonding force resembling a weak spring), hence particles driven by thermal energy are relatively free to move along the interparticle distance R_w. Continuous reordering results in densely packed clusters, for which f approaches 3. Therefore, even when R_{eff} is large, ϕ_{eff} is slightly higher than ϕ. Under these conditions, the emulsion remains fluid and almost Newtonian. To reach the gelation threshold, relatively high values of ϕ are required, as shown in Figure 3.

In contrast, at high values of C_p the secondary minimum becomes more pronounced, narrower and closer to the droplet surface (Figure 1a): $U_w > k_BT$ and k_w is relatively large (bonding force resembling a stiff spring). All of this means that particles trapped in the potential wells are more constrained to move. More precisely, particles stick together to form loosely packed clusters with low internal densities, as illustrated in Figure 1c (box on the right). In this case, the fractal dimension is low (f ~ 2), the effective volume fraction is $\phi_{eff} >> \phi$ and hence $\eta_0 >> \eta_F$. Under quiescent conditions, large clusters become crowded at low ϕ and the gel transition is easily attained (Figure 3). If the emulsion is subjected to flow, the shear forces acting on particles gradually remove them from the potential wells; then clusters break up and the emulsion shear-thins.

CONCLUDING REMARKS

Oil-in-water emulsions are widely used in food technology, as well as in cosmetics and pharmaceutical products. In these systems, it is desirable to attain a rational manipulation of phase transitions and rheology by adjusting the formulation. In order to better understand the connection between the bulk physical properties and the physicochemical parameters of the dispersion, one may use the framework of colloid science and define the following top-down, multiscale picture: macroscopic properties (flow and phase behavior) → microstructure (aggregates morphology) → particle-particle interactions (pair potential) → physicochemical characteristics (surface charge, ionic strength, additives concentration, etc.). In this analytical context, the present work discusses how the nature of the pair interaction influences the aggregation, gelation and viscosity of protein-stabilized emulsions. Although some improvements on the subject need to be made, this knowledge offers new perspectives for the study and design of emulsion-based food systems.

ACKNOWLEDGMENTS

The author wishes to thank SEPCYT-FONCyT (PICT 09-14732), SeCyT-UNL (CAI+D 12/I301) and CONICET, Argentina, for the financial aid received.

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